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AUTHOR(S):

Takahashi, Massahide; Jin, Jisun; Uchino, Takashi; Yoko, Toshinobu

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# Photochemical Reactions of Ge-Related Centers in Germanosilicate Glass Prepared by Sol-Gel Process

Masahide Takahashi, Jisun Jin, Takashi Uchino and Toshinobu Yoko

Germanosilicate glasses are prepared by a sol-gel method and the UV-photosensitivity of glasses is investigated by optical absorption, ESR, and photoluminescence measurements. Large changes in optical absorption are observed for the sol-gel-derived glass by the ultraviolet laser irradiation; a decrease in 5-eV band and increases in absorption around 4.5 and  $> 5.7$  eV. Photoluminescence intensity under 248-nm excitation decreases with an increase in laser fluence and also with decrease in the 5-eV band. This result strongly implies the novel photochemical reaction from  $\text{Ge}^{2+}$  to  $\text{Ge E}'$  induced by excimer laser irradiation.

**Keywords :** Germanosilicate glasses / Defect / Photosensitivity / Sol-gel method / Fiber grating

Photosensitivity of  $\text{GeO}_2$ - $\text{SiO}_2$  glasses has been caught much attention because the Bragg grating can be easily printed in the fiber core, which is usually made of germanosilicate glasses, by ultraviolet (UV) laser irradiation [1]. It has been considered that the index change by UV laser irradiation is closely related to the photochemical processes of Ge-related defects in the germanosilicate glasses [2]. Previous studies indicated that the Ge-related defects have higher photosensitivity and the formation of Ge E' center is the key for the photorefractive effect in the glasses. In order to investigate the mechanism of UV induced refractive index change, the compositional and/or structural effect on the photochemical processes should be systematically clarified. The aim of this study is to elucidate photochemical processes induced by UV-irradiation in the germanosilicate glass.

The defect states of glasses before and after the UV

irradiation (KrF- and ArF-excimer lasers and Hg lamp) are analyzed by means of the optical absorption, photoluminescence (PL) and electron spin resonance (ESR) spectroscopy. Germanosilicate glass of  $10\text{GeO}_2$ - $90\text{SiO}_2$  composition in molar ratio is prepared from tetraethoxysilane and tetraethoxygermanium through the sol-gel procedure.

Figure 1 shows the changes in optical absorption by the KrF irradiation. Change in optical absorption in the range of 3.8 to 6.4 eV is observed. The change in optical absorption of the glass seems to be almost comparable to that of the VAD fiber preform. ESR spectra after excimer laser irradiation indicate the existence of germanium electron-trapped centers (GEC) and Ge E' center. Fig. 2 (e) shows the ESR spectrum of unirradiated VAD-glass, which is corresponding to Ge E' center [3]. Spectral profile of low fluence (Fig. 2 (a)) indicates the formation of

## SOLID STATE CHEMISTRY -Amorphous Materials-

### Scope of Research

*Inorganic amorphous materials with various functions are the targets of research in this laboratory. (1) To obtain a clear view of glass materials and the bases for designing functional glasses, we investigate the structure of glasses using X-ray and neutron diffraction analysis, high resolution MAS-NMR, and ab initio MO calculation. (2) To develop materials with high optical nonlinearity, we search heavy metal oxide-based glasses and transition metal oxide thin films, and evaluate the nonlinear optical properties by Z-scan methods. (3) Photosensitivity of glasses for optical fibers and waveguides is investigated to design efficient fiber gratings and optical nonlinear materials. (4) Using sol-gel method, synthesis and microstructure control are carried out on various functional oxide thin films.*



Prof  
YOKO,  
Toshinobu  
(D Eng)



Instr  
UCHINO,  
Takashi  
(D Eng)



Instr  
TAKAHASHI,  
Masahide  
(D Sc)



Assoc. Instr  
JIN,  
Jisun  
(D Eng)

### Guest Research Associates:

ZHAO, Gaoling (D Eng)

### Students:

SAKIDA, Shinichi (DC)  
TAKAISHI, Taigo (DC)  
TOKUDA, Youmei (DC)  
NIIDA, Haruki (MC)  
TATSUMI, Masao (MC)  
MIYAWAKI, Seikyo (MC)  
KAJITA, Daisuke (MC)  
HIROSE, Motoyuki (MC)  
KUBO, Akiko (UG)  
TSUKIGI, Kaori (UG)  
TAKEUCHI, Toshihiro (UG)  
DORJPALAM, Enkhtuvshin (RS)

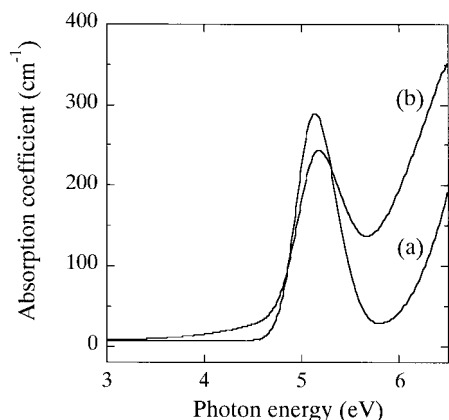


Figure 1. Absorption spectra before and after KrF laser irradiation (80 mJ/cm<sup>2</sup> per pulse, 10<sup>4</sup> shot)

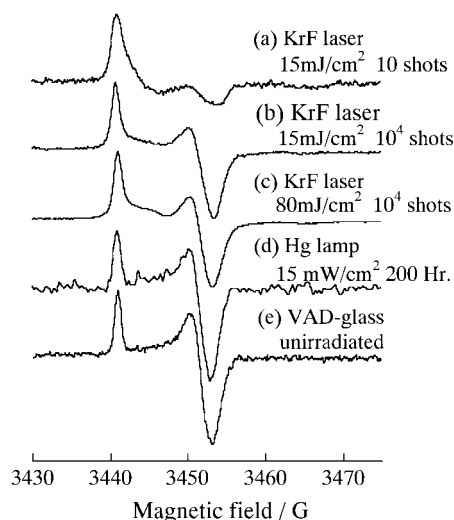


Figure 2. ESR signals of the glasses after UV irradiation and unirradiated fiber preform.

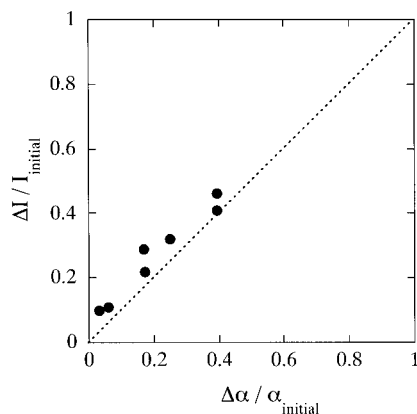


Figure 3. Correlation between decrease in PL intensity,  $\Delta I/I_{\text{initial}}$ , and bleaching of the 5-eV band,  $\Delta\alpha/\alpha_{\text{initial}}$ , by excimer laser irradiation.

GEC [4]. With increasing laser fluence, the profile approaches to that of Ge E' center (Fig. 2 (a) to (c)). Irradiation of an Hg lamp induced only Ge E' center (Fig. 2 (d)).

Figure 3 shows a correlation between the bleaching of 5-eV band and the decrease in PL intensity by KrF laser

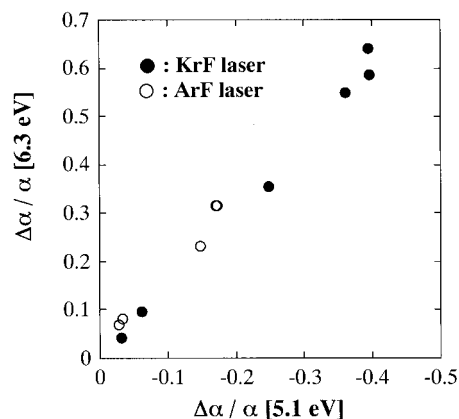
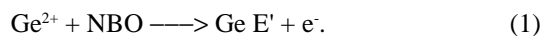


Figure 4. Changes in absorption coefficient of the 5-eV band and 6.3 eV band.

irradiation. Linear correlation indicates that bleaching of the 5-eV band is due mainly to a decrease in Ge<sup>2+</sup> (NODV). This relationship is also exhibited by ArF-laser excitation. Therefore, we propose that the bleaching of the 5-eV band by irradiating excimer laser is due to the decrease of Ge<sup>2+</sup>.

The decrease of Ge<sup>2+</sup> by excimer laser irradiation would be explained by photoionization of Ge<sup>2+</sup> by multiphoton absorption. The lone pair electron of Ge<sup>2+</sup> can be excited to the conduction band by successive two-photon absorption through long-lived T<sub>1</sub> state as an intermediate level. Furthermore, the ionized Ge<sup>2+</sup> may form Ge-O bonding with nonbridging oxygen nearby. The final product of this process would be Ge E'. Fig. 4 shows a correlation between the decrease in the 5-eV band and the increase in 6.3 eV band corresponding to Ge E' center by irradiating KrF and ArF laser. The linear correlation indicates that Ge<sup>2+</sup> is converted into Ge E' by excimer laser irradiation. In addition, changes in defect concentration of Ge<sup>2+</sup> and Ge E' are almost equal. Therefore, we propose the following photochemical reaction by excimer laser excitation,



The conversion efficiency of Ge<sup>2+</sup> to Ge E' is much larger for KrF laser excitation than for ArF laser at the same fluence. The photon energy of KrF laser agrees with the excitation energy of S<sub>0</sub> to S<sub>1</sub> transition in Ge<sup>2+</sup>. The excited S<sub>1</sub> state relaxes to long-lived T<sub>1</sub> state through intercombinational conversion. These facts follow the above reaction (1) because the 5-eV photons from KrF laser excite Ge<sup>2+</sup> to long-lived T<sub>1</sub> state with higher efficiency than 6.3-eV photons from ArF laser.

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